Surface Tension as Related to Crystal Growth

Senior Thesis
Presented in Addition to the
Requirements for the Degree
Bachelor of Arts

by
Kathy Paul

The Ohio State University
1975

Approved

Advisor
Department of Geology
and Mineralogy

Table of Contents

Acknowledgements

I wish to thank first of all Dr. Dan McLachlan for his suggestion of the project, his guidance while it was being conducted, and his patience with the many delays in concluding it. I wish to thank Dr. Sidney E. White for giving me the confidence to attempt a senior thesis. I wish to thank my parents most of all, for without them none of this would have been possible.

Introduction

The research upon which this paper is based was designed as an investigation into the force of surface tension and how it relates to crystal growth. Included are not only the results found by this author, but those of another author (Pappenhumer) to show a slightly different aspect of surface tension and how it affects something other than a crystal, in this case some amino acids.

Description of Equipment

The equipment used in researching this thesis was built by Dr. Dan McLachlan Jr., and centered around two main pieces of apparatus. One piece was a modified Leitz microscope, used for making actual measurements. The other piece was a capillary tube-squeeze bulb apparatus, through which various solutions were drawn upward to be measured.

A capillary tube of .50 millimeter bore was used as an area that the molecules of the various solutions could adhere to. One end of the capillary tube was placed in a 20cc test tube which contained the solutions used. The capillary tube was held stationary in the test tube by means of a rubber stopper. The base of the test tube was placed in a bracket so that the whole test tube remained stationary during the course of the research. To the other end of the capillary tube was attached a rubber squeeze bulb which could be used to draw the solutions up from the test tube into the capillary tube. The rubber squeeze bulb was held in place by means of a clamp attached to a ringstand. This also helped to hold the other end of the capillary tube stationary.

The tube of a Leitz microscope was removed from its base and mounted on a device permitting it to be racked up and down by merely turning a knob. This was calibrated in accordance with a centimeter scale. Measurements accurate to the third decimal place were made possible by dividing the knob, already accurate to the second decimal place, into tenths. The microscope was placed on one side of a tube and a light was placed directly opposite the lense of the microscope on tje other side of the test tube. It should be noted at this

point why and how it is possible to see the level in the capillary tube. The light rays will shine through the air and be refracted off the capillary because of the difference of index of refraction between glass and air. This area will appear dark through the microscope. The light rays coming directly through the liquid in the capillary bore will not be refracted because of the index of refraction of the liquid. This area will appear bright.

The solutions, once mixed, were poured into a 50ml buret tube, from which they could be accurately measured. For convenience the buret tube was attached by means of a clamp to the same ringstand that the rubber squeeze bulb was clamped.

Description of Procedure

For each solute used two different resourcinol solutions were mixed: a 10% resourcinol solution and a 20% resourcinol solution. This was done by measuring 100ml of a particular solute into a beaker and dissolving 10g or 20g of resourcinol into the beaker to make ita 10% or 20% solution, respectively. When the solution was mixed it was then poured into the buret tube. From the 10% resourcinol solution could be gotten anywhere from a 1% to 10% solution simply by measuring out .1ml of solution for a 1% solution, .2ml of solution for a 2% solution and so forth on up to 1.0ml of solution for a 10% solution. This same principle was applied for 11% to 20% solutions using a 20% resourcinol solution. 0% concentrations of each solution were measured using pure solute.

Once the correct amoung of solution was measured out of the buret into the test tube, the capillary tube was placed in the test tube with the end of it under the level of the liquid. The microscope was lowered to the level of the liquid, the light was turned on, and the level was measured and redorded. The solution was then drawn up the tube several times to thoroughly wet the inside of the capillary and make adhesion of the molecules of the solution to the capillary possible. To draw as olution up the capillary, the bulb was squeezed in the hand with the thumb placed over the air hole on the end of the squeeze bulb. Once the liquid was drawn completely up the tube, the squeeze bulb was allowed to expand but still keeping the thumb over the air hole. This permitted the solution to fall to a certain height in the capillary which was measured

by the microscope. Each concentration of each solution was measured three times to get an average height, and insure greater accuracy of measurement.

After each concentration was measured it was emptied out of the test tube and a new concentration was put in. During this time the test tube and capillary tube were thoroughly cleaned with a laboratory cleaning agent and distilled water to prevent any contamination. All glassware was thoroughly cleaned before and after use and every time the solution was changed.

Presentation and Interpretation of Raw Data

The percent resourcinol solution (concentration), the three heights measured for each concentration along with the average height, K_r(the derivation and meaning of which is discussed below), and calculated surface tension are represented in the following data tables. The data is arranged in tabular form under the different solutes. Included with each solute is its chemical formula and the density used to calculate the surface tension(both taken from The Handbook of Chemistry and Physics,1973)
The graphs represent the calculated surface tension plotted against the resourcinol concentration in gm/ml. All surface tensions have been calculated from this author's data and if they vary from any figures already reported in the literature it is because of experimental error.

The measurements made using acetone were plotted on a different graph because of the unusual results. All results were double checked to make sure they were accurate. This author has no explanation for these results.

The author of this paper has come to the conclusion that density does not account for the differences in height in the capillary tube.

Distilled Water H_2O

Density 1.0000

%Resourcinol	First Height	Second Height	Third Height	Average Height	K_r	Gamma
0%	7.938	7.938	7.938	7.938	9.07	71.997
5%	8.572	8.572	8.585	8.577	9.07	77.793
6%	8.577	8.575	8.580	8.577	9.07	77.793
7%	8.719	8.722	8.724	8.722	9.07	79.108
8%	8.722	8.724	8.724	8.724	9.07	79.126
9%	9.146	9.146	9.154	9.149	9.07	82.928
10%	9.606	9.652	9.791	9.677	9.07	87.770
12%	9.596	9.601	9.601	9.601	9.07	87.081
15%	9.601	9.606	9.601	9.601	9.07	87.081

Methyl Alcohol CH_3OH

Density .7914

%Resourcinol	First Height	Second Height	Third Height	Average Height	K_r	Gamma
0%	3.921	3.920	3.922	3.920	19.38	76.017
1%	3.941	3.941	3.941	3.941	19.38	76.365
2%	3.960	3.963	3.965	3.963	19.38	76.773
3%	3.998	3.997	3.999	3.998	19.38	77.021
4%	4.000	4.000	4.000	4.000	19.38	77.322
5%	4.057	4.055	4.060	4.057	19.38	78.573
10%	4.124	4.122	4.126	4.124	19.38	80.976
15%	4.261	4.262	4.260	4.261	19.38	82.700
20%	4.320	4.321	4.320	4.320	19.38	83.803

Ethyl Alcohol CH_3CH_2OH

Density .7893

%Resourcinol	First Height	Second Height	Third Height	Average Height	K_r	Gamma
0%	4.079	4.089	4.084	4.084	19.33	78.943
1%	4.132	4.132	4.127	4.132	19.33	79.871
2%	4.122	4.114	4.117	4.117	19.33	79.581
3%	4.135	4.132	4.130	4.132	19.33	79.871
4%	4.119	4.132	4.132	4.130	19.33	79.832
5%	4.094	4.094	4.112	4.104	19.33	79.330
10%	4.452	4.455	4.452	4.452	19.33	86.057
15%	4.607	4.612	4.612	4.612	19.33	89.149
20%	4.759	4.742	4.759	4.759	19.33	91.991

Isopropyl Alcohol CH_3CH_3CHOH

Density .7855

%Resourcinol	First Height	Second Height	Third Height	Average Height	K_r	Gamma
0%	4.729	4.729	4.729	4.729	19.24	90.001
1%	4.730	4.731	4.729	4.730	19.24	90.702
2%	4.780	4.781	4.780	4.780	19.24	92.004
3%	4.875	4.870	4.880	4.875	19.24	93.850
4%	4.922	4.922	4.921	4.922	19.24	94.742
5%	4.999	5.000	4.998	4.999	19.24	96.103
10%	5.140	5.145	5.135	5.140	19.24	100.015
15%	5.285	5.283	5.287	5.285	19.24	101.760
20%	5.322	5.321	5.322	5.322	19.24	102.403

Butyl Alcohol $CH_3CH_2CH_2CH_2OH$

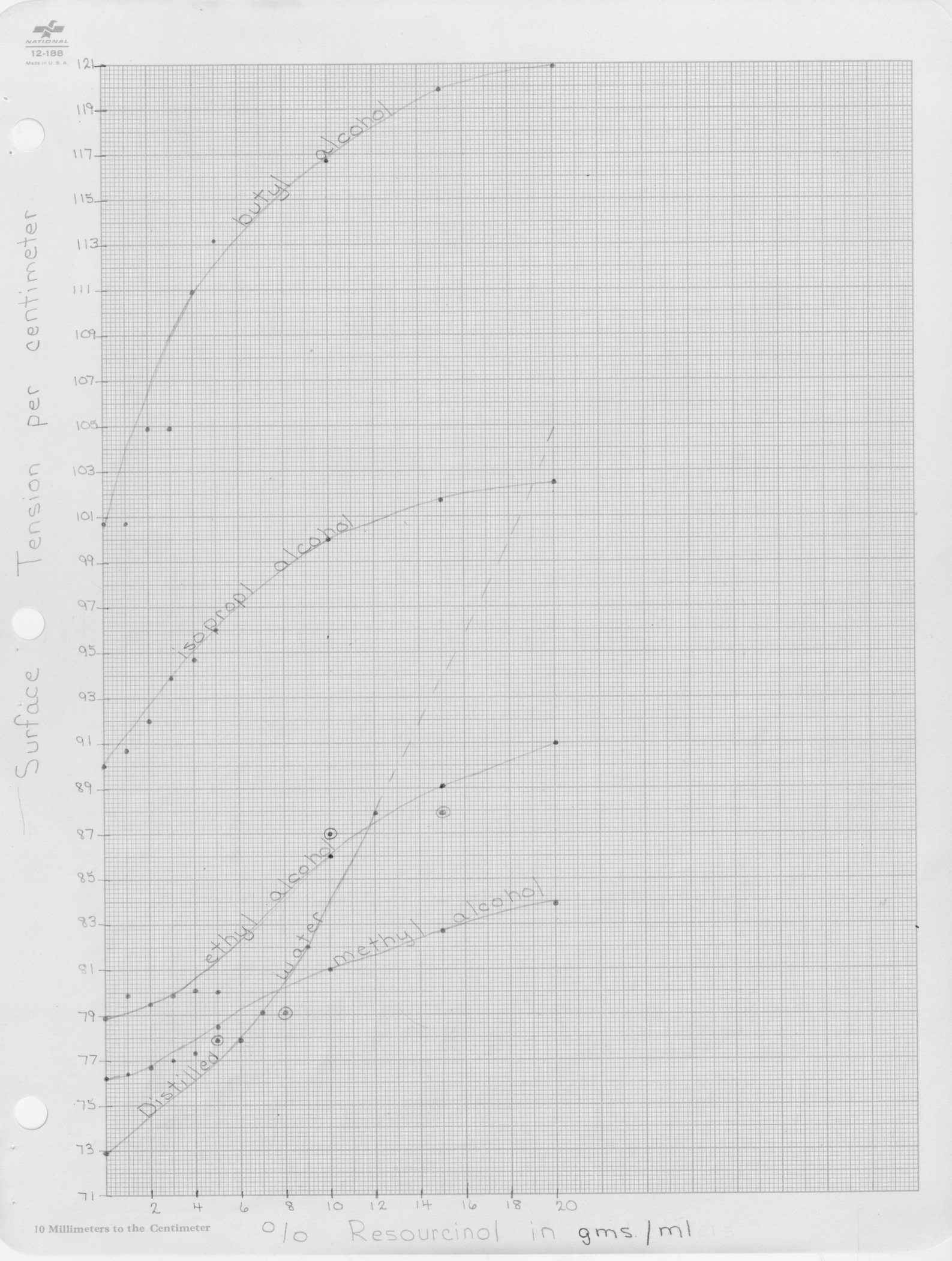
Density .809

%Resourcinol	First Height	Second Height	Third Height	Average Height	K_r	Gamma
0%	5.080	4.851	5.080	5.080	19.82	100.68
1%	5.080	5.080	5.080	5.080	19.82	100.68
2%	5.384	5.397	5.410	5.397	19.82	104.96
3%	5.397	5.397	5.397	5.397	19.82	104.96
4%	5.624	5.624	5.637	5.627	19.82	110.90
5%	5.715	5.702	5.715	5.712	19.82	113.21
10%	5.842	5.969	5.969	5.918	19.82	116.74
15%	6.045	6.045	6.045	6.045	19.82	119.81
20%	6.096	6.121	6.096	6.103	19.82	120.96

Acetone $(CH_3)_2CO$

Density .792

%Resourcinol	First Height	Second Height	Third Height	Average Height	K_r	Gamma
0%	4.445	4.457	4.470	4.457	19.40	86.465
10%	4.775	5.080	5.087	4.927	19.40	96.783
20%	5.232	5.308	5.126	5.232	19.40	101.500
30%	4.698	4.800	4.800	4.800	19.40	93.120
40%	4.826	4.800	4.851	4.826	19.40	94.109
50%	4.851	4.851	4.826	4.851	19.40	94.624


NATIONAL
12-188
Made in U. S. A.
Surface Tension per centimeter
121
119
117
115
113
111
109
107
105
103
101
99
97
95
93
91
89
87
85
83
81
79
77
75
73
71
butyl alcohol
isopropl alcohol
ethyl alcohol
methyl alcohol
Distilled water
2
4
6
8
10
12
14
16
18
20
10 Millimeters to the Centimeter
% Resourcinol in gms./ml

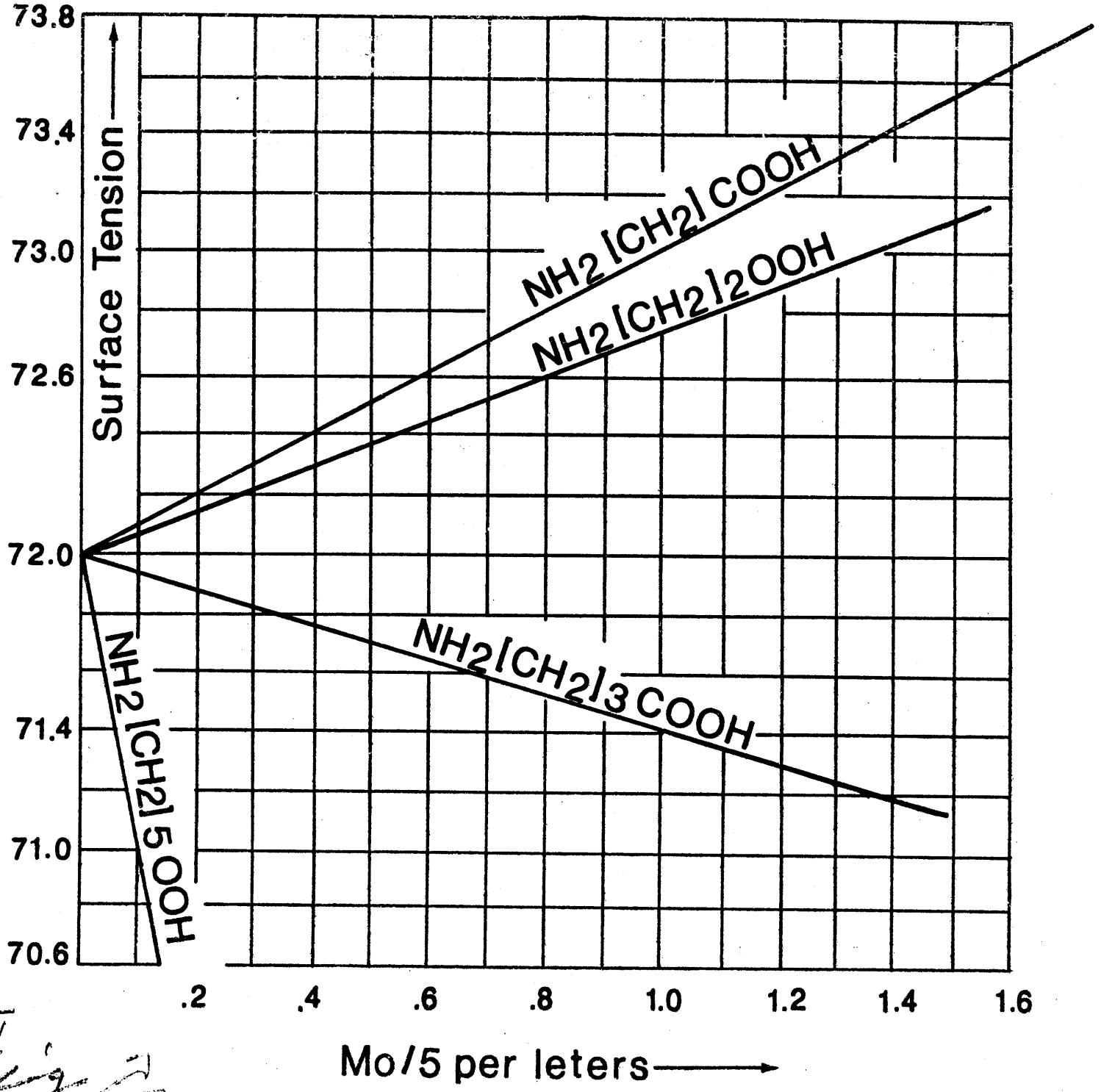

73.8
73.4
73.0
72.6
72.0
71.4
71.0
70.6
Surface Tension
NH2[CH2]COOH
NH2[CH2]2OOH
NH2[CH2]3COOH
NH2[CH2]5OOH
.2
.4
.6
.8
1.0
1.2
1.4
1.6
Mo/5 per leters

Fig 2

Discussion of Mathematic Theory and Calculations

The following mathematical statement can be used as the background for calculating surface tension (McLachlan,1975) :

(force upward) $2\pi r\gamma\cos\theta = \pi r^2 hdg$ (the force downward)

where: r = diameter of capillary bore
γ = surface tension
h = height the solution rises in the tube
d = density of the solute
g = gravitational constant, 980 cm/sec^2

The equation can be rewritten:

$$2\gamma\cos\theta = hdgr$$

rearranging,

$$\gamma = \frac{hdgr}{2\cos\theta}$$

if $\theta = 0^\circ$, then $\cos\theta = 1$

the term $\frac{dgr}{2}$ can be expressed as K_r, a constant for each concentration of a solution. Our equation now looks like this:

$$\gamma = hK_r$$

The surface tension of pure water can be approximated at 72. Using this value we can determine K_r for each solution.

$$K_r = \frac{72}{h} \quad \text{for water}$$

where h is the height measured of each solute with a 0% resourcinol concentration. Once K_r is calculated for each solute, it can be used to calculate the surface tension for each concentration of the solutions measured.

$$\gamma = hK_r$$

where K_r is the same for all concentrations of a particular solution. h is the average height measured for each particular concentration.

Discussion of Surface Tension

Alexander defines surface tension of a liquid as "the force exerted at right angles across a line of unit length on the surface of the liquid when it is in contact only with its own vapor."[4] A drop of liquid is subject to three pulls: 1) the surface tension of water against the air which tends to drag out the rim and make the rim flatter and flatter, 2) the surface tension of liquid against water, and 3) the surface tension of liquid against air which have the effect of pulling the rim in and making the drop more and more spherical. Each case depends on the balance between these pulls. It has been proven experimentally that if a disssolved substance lowers the surface tension of the solvent, the solute tends to concentrate at the boundary layers because the potential energy of the system strives toward a minimum.[1]

One of the methods used to measure surface tension is the capillary rise method in which the interior of the capillary tube would be covered with a liquid. The surface tension tries to reduce this large surface. Consequently the liquid rises. There is an equilibrium present when the force of surface tension acting upwards balances the weight of the column of liquid.[2]

A graph from Pappenhumer is included for comparison with the graph drawn up form this research. Pappenhumer's graph shows the effect of amino acids on surface tension in a water solution.[4] (Figure 2).

As stated before, the capillary rise method was used in this research to measure surface tension. Another method has been reported which, although used to measure interfacial tensions using volatile solvents, can possibly be used to

measure surface tension. The method used is the iverted bubble. Measurements can be taken which can be used in calculating surface tension.[5]

Conclusion

It follows from the previous discussion of surface tension that if the surface tension is decreased or at a minimum on a particular surface (a crystal, for example) that surface should be permitted to grow.[4] If surface tension is kept at a minimum, the crystal should have unlimited growth. Since it is known that molecules orient themselves near the surface of a solution, this provides room for the crystal to grow in solution. Before a solute actually forms into a crystal it forms into an amorphous group. This aggregates into spherulites by tension between the members of the amorphous group. These molecules in the spherulites reorient into crystals.[1] The solution from which a crystal is being formed will contribute to growth with reduction in surface tension. The surface tension on the spherulites of solute will prevent them from breaking away from the crystal. The force of the surface tension will shield the drop of solution, thus helping the solute in the spherulite adhere to the crystal. Since a higher surface tension indicates more molecules along the surface, it also indicates a stronger surface for a crystal to grow under, thus providing a form of protection for the crystal. Thus, one can see that surface tension does affect crystal growth and that the amount of surface tension of each solution, since it varies, affects crystal morphology differently for each solution.

Bibliography

Bibliography

1. Alexander, Jerome "Colloid Chemistry" 4th ed., W. Van Nostrand & Co. New York 1937

2. Freundlich, Herbert "Colloid and Capillary Chemistry" E. P. Dutton & Co. New York 1922

3. Harkins, William D. "The Physical Chemistry of Surface Films" Reinhold Publishing Co. New York 1952

4. McLachlan, Dan Jr. Preprint to American Mineralogist 1974

5. McLachlan, Dan Jr. and Cox, Herbert M. "Apparatus for Measuring the Contace Angles at Crystal-Solution-Vapor Interfaces" Rev. Sci. Instrum., Vol. 46, No. 1, January 1975